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New blue fluorescent sensors for metal cations and protons based on 1,8-naphthalimide

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Abstract

Monomeric 1,8-naphthalimide in acetonitrile was found to respond to the presence of metal cations (Zn^{2+}, Pb^{2+}, Cu^{2+} and Fe^{3+}) via enhancement of its fluorescence intensity; in the nonpolar solvent, tetrahydrofuran, the response was negligible, regardless of the nature of the cations used. When 1,8-naphthalimide was copolymerised with styrene, the ensuing high M_r polymeric chemosensor reacted selectively to the addition of Fe^{3+} cations. The finding that the fluorescence intensity of this high M_r sensor increased in acidic media due to protonation of the *N*,*N*-dimethylamino receptor groups, suggests that it may offer potential as a reusable sensor for water pollution by Fe^{3+} cations and protons.

Keywords: 1,8-Naphthalimide; Blue fluorescent polymer; Sensor; Environment; PET; Metal cations; Protons

1. Introduction

The environmental impact of heavy metal cations is a major environmental protection issue. In this context, of particular interest are fluorosensors, which are molecular devices capable of detecting the presence of environmental pollutants via changes in their spectral characteristics [1−3].

Chemosensors are of two types, namely low M_r compounds and polymers (both linear and star-shaped) [4,5]. Fluorescent polymeric materials have features that enable them to act as highly sensitive chemosensors for heavy metal cations. Polymeric fluorosensors are of particular interest because they are molecular devices powered by light and which possess high sensitivity to various external signals. The functional characteristics of polymeric fluorosensors can be expressed either by conformational changes of the macromolecules or by collective transport properties. It has been shown that the photoinduced electron transfer (PET) that proceeds in 1,8-naphthalimide also takes place in the solid polymeric films of its copolymers derived from conventional commercial monomers. Hence, the copolymers can also be sensors for transition metal ions or protons [6−10]. In all cases, the fluorophores are sufficiently thermo- and water-resistant to allow the copolymers to be used for cation detection in solution; in the solid state, copolymeric sensors are reusable.

Fluorescent PET sensors are of great interest because of their various applications. Under appropriate conditions, the fluorophore emission is quenched by the distal amine group with at least partial electron transfer from the amine group to the fluorophore ring. If the PET process is ‘‘switched off’’ by, for example, protonation of the amine group or by their complexation with metal ions, the fluorescence of the fluorophores is restored.

This paper concerns the functional characteristics of a novel, blue fluorescent monomeric 1,8-naphthalimide and of its copolymer with styrene and the prospects to use the

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newly synthesized materials as efficient and selective sensors for metal cations and protons in both solution and in the solid state.

2. Experimental

The synthesis of the monomeric 2-allyl-6-(2-dimethylaminoethyloxy)-benzo[*d*,*e*]isoquinoline-1,3-dione (MD) and its copolymer with styrene (Scheme 1) has been described recently [10].

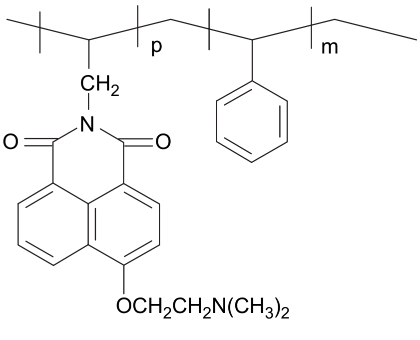
UV–vis spectrophotometric investigations were performed using a *Uvikon 930* spectrophotometer (Kontron instruments). Fluorescence spectra were taken on a Jasco *FP-6500* spectrofluorometer. Fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra, using anthracene as reference ($\Phi_{st} = 0.26$). All absorption and fluorescence measurements were carried out at 10^{-5} mol l^{-1} MD; the polymer concentration in solution for all measurements was 5 g l^{-1}. The effect of the metal cations and protons on fluorescence intensity was examined by adding a few microlitre of stock solution ($c = 10^{-2}$ mol l^{-1}) of the metal cations to a known volume of the ligand solution (3 ml). This addition was limited to 0.08 ml, so that dilution remained insignificant [11]. $Cu(NO_3)_2 \cdot 3H_2O$, $Pb(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot H_2O$ and $Zn(NO_3)_2 \cdot 4H_2O$ were investigated as sources for metal cations. For all absorbance and fluorescence measurements the polymer film was placed diagonally into the sample quartz cuvette to improve measurement reproducibility.

3. Results and discussion

3.1. Spectral characteristics of monomeric and polymeric fluorophores

The functional properties of MD were investigated in two organic solvents of different polarity, namely acetonitrile ($\varepsilon = 37.5$) and tetrahydrofuran ($\varepsilon = 7.58$) at 1×10^{-5} mol l^{-1}. Table 1 summarizes the basic photophysical characteristics of MD – absorption (λ_A) and fluorescence (λ_F) maxima, Stokes shift ($\nu_A - \nu_F$), oscillator strength (f), quantum yield of fluorescence (Φ_F) and energetic yield of fluorescence (E_F).

In acetonitrile and tetrahydrofuran, MD is colourless with absorption maxima in the near UV region at $\lambda_A = 366$ and 363 nm. In both solvents, MD emits a blue fluorescence with well-defined maxima at $\lambda_F = 436$ and 429 nm, respectively. The calculated Stokes shift values were 4368 cm^{-1} for the spectra in acetonitrile and 4238 cm^{-1} for those in tetrahydrofuran. It was observed that in the less polar medium, the value of Stokes shift was lower than that obtained in the more polar medium (Table 1). The Stokes shifts obtained were very similar to those of other, similar monomeric 1,8-naphthalimide dyes [12].



Scheme 1. Schematic presentation of poly(St-*co*-MD).

The quantum fluorescence yield of MD in both organic solvents was calculated on the basis of the absorption and fluorescence spectra using Eq. (1):

$$\Phi_F = \Phi_{st} \frac{S_u}{S_{st}} \frac{A_{st}}{A_u} \frac{n_{Du}^2}{n_{Dst}^2} \tag{1}$$

where Φ_{st} is the quantum yield of the reference, A_{st} and Au represent the absorbance of the reference and the sample, respectively, S_{st} and S_u are the integrals of the emission of the reference and the sample, respectively, and n_{Dst} and n_{Du} are the refractive index of the reference and the sample, respectively. In acetonitrile solution, the quantum yield was low, $\Phi_F = 0.009$, while in tetrahydrofuran solution, a value some 88 times higher was obtained ($\Phi_F = 0.796$). This significant difference is due to photoinduced electron transfer (PET) that was quenched in nonpolar medium causing restoration of fluorescence.

Besides Φ_F, the energy yield of fluorescence (E_F) can also be used to characterize the fluorescence efficiency of MD [13].

$$E_F = \Phi_F \lambda_A / \lambda_F \tag{2}$$

E_F values of 0.008 and 0.673 were secured for acetonitrile and tetrahydrofuran, respectively.

The spectral characteristics of poly(St-*co*-MD) in the solid state are of interest in order to evaluate this copolymer as a heterogeneous fluorescent sensor. The copolymer was transparent and colourless, emitting blue fluorescence. The excitation and fluorescence spectra of poly(St-*co*-MD) in the solid state as a thin polymer film ($d = 40$ μm) is presented in Fig. 1 from which it is evident that the excitation and fluorescence spectra have bands with a single maximum, without vibrational structure and with well-defined maxima at 371 and 434 nm, respectively. The fluorescence maximum of poly(St-*co*-MD) was similar to that of MD. The spectral characteristics of the former reveal that the chemical structure of the chromophoric system does not change its conformation in the solid state.

3.2. Effect of the metal cations on the fluorescence intensity of MD in acetonitrile and tetrahydrofuran

The photophysical properties of MD as a ligand in the presence of different metal cations (Zn^{2+}, Pb^{2+}, Cu^{2+} and Fe^{3+}) were investigated in acetonitrile and tetrahydrofuran solution in view of its potential sensor application. Prior to assessment, the sensor ability of the monomer bonded to a polystyrene chain was determined.

Table 1
Photophysical characteristics of MD in acetonitrile and tetrahydrofuran solutions

	λ_A/nm	ε/l mol^{-1} cm^{-1}	λ_F/nm	$\nu_A - \nu_F$/cm^{-1}	f	Φ_F	E_F
Acetonitrile	366	14 700	436	4368	0.68	0.009	0.008
Tetrahydrofuran	363	16 200	429	4238	0.74	0.796	0.673

Acetonitrile was chosen as solvent for all spectral measurements as it has a low quantum florescent yield and favours the PET fluorescence switch. In contrast, the solvent guaranties good solubility of the metal salts, ligand and the respective complexes. Tetrahydrofuran was used as a solvent for both MD and poly(St-*co*-MD) fluorophores.

The influence of the metal cation on the fluorescence intensity of MD alone was measured in both acetonitrile and tetrahydrofuran. A dramatic enhancement of fluorescence intensity in the presence of the guest metal cations was only observed in the case of acetonitrile. The influence of the metal cations on fluorescence enhancement (FE) is presented in Fig. 2 ($FE = I/I_0$ was determined from the ratio of maximum fluorescence intensity I – after the addition of metal cation – and minimum fluorescence intensity I_0 – before metal cation addition). The values of FE followed the order: $Fe^{3+} > Zn^{2+} > Cu^{2+} > Pb^{2+}$.

In the absence of metal cations, the low fluorescence emission of MD in acetonitrile can be attributed to an efficient PET process that takes place between the photoexcited 1,8-naphthalimide and the lone-pair electrons of the free amine In the presence of metal cations, the lone-pair electron of the tertiary amine quencher is engaged in coordination with metal cations. (Scheme 2).

Once engaged in such coordination with metal cations, the former lone-pair electrons of the amine can no longer serve as efficient quenchers of the photoexcited 1,8-naphthalimide fluorophore, since they are stabilized in the form of a σ bond. When bound to the metal cation, MD emits intensive fluorescence.

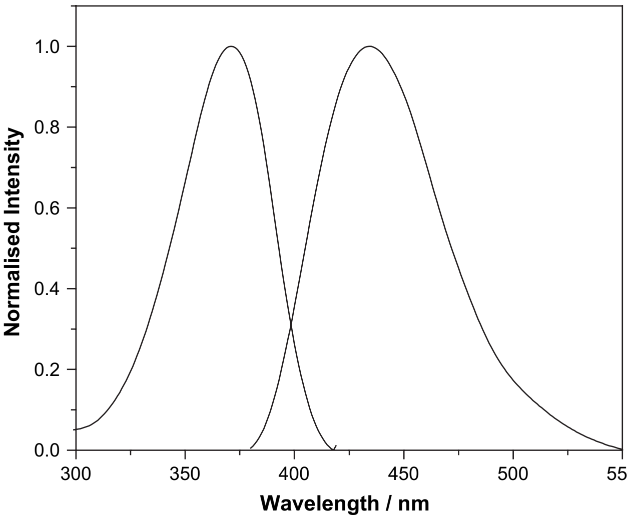


Fig. 1. Excitation and fluorescence spectra of poly(St-*co*-MD) in solid state.

In tetrahydrofuran solution the low fluorescence enhancement (FE = 1.3–2.2) can be assigned to the nonpolar nature of the solvent and to the high quantum fluorescence yield. In this case, the effect of complex formation between the metal ions and the 1,8-naphthalimide is suppressed as the polarity of the solvent quenches the PET. Hence, this solvent is not good for investigating the sensor capacities of the newly synthesized MD.

The change in the fluorescence intensity of MD induced by Fe^{3+} is shown in Fig. 3 as an example. The increase in fluorescence intensity imparted by addition of Fe^{3+} is clearly concentration-dependent insofar as $>10^{-4}$ mol l^{-1}, the fluorescence intensity decreased due to the so-called concentration fluorescence quenching. The Fe^{3+} cations induce a hypsochromic shift $\Delta\lambda_F = 10$ nm to the fluorescence maximum ($\lambda_F = 426$ nm) showing that the switch might bind metal cations to the nitrogen atoms from the receptor via a chelation [14].

The basic photophysical characteristics obtained for MD in acetonitrile solution in the presence of all of the metal cations under study is presented in Table 2.

Table 2 shows that no change in the absorption maxima occurred in comparison with MD in the absence of metal ions. The metal cations induced a small hypsochromic shift of the fluorescence maxima ($\Delta\lambda_F = 6$–10 nm) implying possible interaction between the MD and metal cations [15]. The results also show the high increase in fluorescence induced by the metal cations. The quantum yield ($\Phi_F = 0.73$–0.86) also increased, compared to that of solutions free of cations

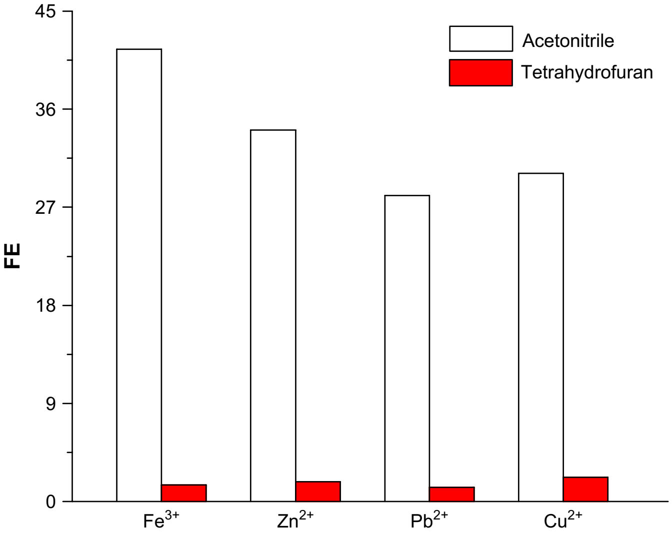
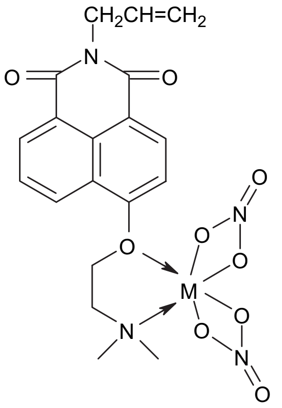


Fig. 2. Fluorescence enhancement factor (FE) of MD ($c = 1 \times 10^{-5}$ mol l^{-1}) in the presence of different metal cations ($c = 5 \times 10^{-5}$ mol l^{-1}) in acetonitrile and tetrahydrofuran.



Scheme 2. Schematic presentation of coordination of MD with metal cations.

($\Phi_F = 0.009$); the highest quantum yield was obtained in the presence of Fe^{3+} cations ($\Phi_F = 0.86$). The higher quantum yield can be ascribed to the superior coordination ability of the Fe^{3+} cations as well as to stabilization of the coplanar system of the complex formed. The spectrum of the MD complex with metal cations had a Stokes shift smaller than that of MD alone, showing the stabilized planarity of the chromophoric structure after complexation. In this case, the non-radiative emission during the transition from S_1 to the ground state S_0 is smaller and leads to the higher fluorescence quantum yield observed.

Table 2
Photophysical characteristics of MD in acetonitrile in the presence of metal cations

Metal cations	λ_A/nm	λ_F/nm	$\nu_A - \nu_F$/cm^{-1}	$\Delta\lambda_F$/nm	Φ_F	E_F
Zn^{2+}	368	430	3918	6	0.81	0.69
Pb^{2+}	368	428	3809	8	0.76	0.65
Cu^{2+}	368	428	3809	8	0.73	0.63
Fe^{3+}	368	426	3699	10	0.86	0.74

3.3. Effect of metal cations on the fluorescence intensity of the poly(St-co-MD) in the solid state

The effect of the metal cations on fluorescence intensity when measured in a thin polymer film of 40 μm thickness was also investigated; the polymer film was immersed in a buffered aqueous solution ($CH_3COOH/NaCH_3COO^-$ at pH = 5.0). The metal cations quenched fluorescence intensity. The rigid polymer structure of the poly(St-*co*-MD) film hindered the contact between the metal cations and the fluorophore receptors. Hence, poly(St-*co*-MD) needed a longer time to display its sensor abilities than homogeneous sensors. The fluorescence emission in the presence of metal cations at $c = 10^{-4}$ mol l^{-1} was investigated for 20 min (Fig. 4). It is evident that the important factor is the nature of the metal cation added. The copolymer film reacted only to the presence of Fe^{3+} ions. The addition of metal cations decreased fluorescence intensity, this being most pronounced in the course of the first 10 min, after which time, fluorescence intensity remained little changed. In the case of Pb^{2+}, Cu^{2+} and Zn^{2+} cations the effect on fluorescence intensity was negligible (2–3%). Fe^{3+} at the same concentration quenched ca. 45% of the fluorescence intensity of the poly(St-*co*-MD). The absence of significant fluorescence quenching by Pb^{2+}, Cu^{2+} and Zn^{2+} cations in aqueous solution renders poly(St-*co*-MD) a highly useful Fe^{3+} selective sensor, especially as this high selectivity of the copolymer for Fe^{3+} was secured in the presence of other important metal cations at the same concentration of the Fe^{3+} ions. Most probably, the Fe^{3+} cations were more competitive in complex formation and nullified the complexation ability of the other cations present.

The different effects of the metal cations on fluorescence intensity of MD in solution (monomer) and in the solid state poly(St-*co*-MD) in terms of sensor application can be explained by differences in the density and flexibility of the

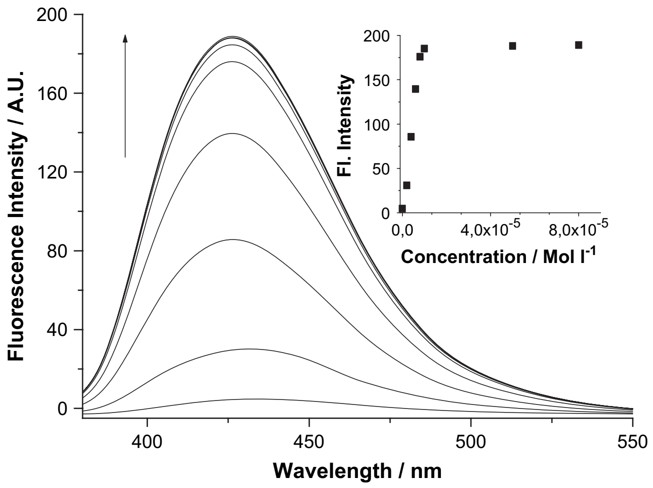


Fig. 3. Fluorescence spectra of MD in acetonitrile at various Fe^{3+} concentrations, increasing from 0 to 1×10^{-4} mol l^{-1}; the concentration of MD was 1×10^{-5} mol l^{-1}.

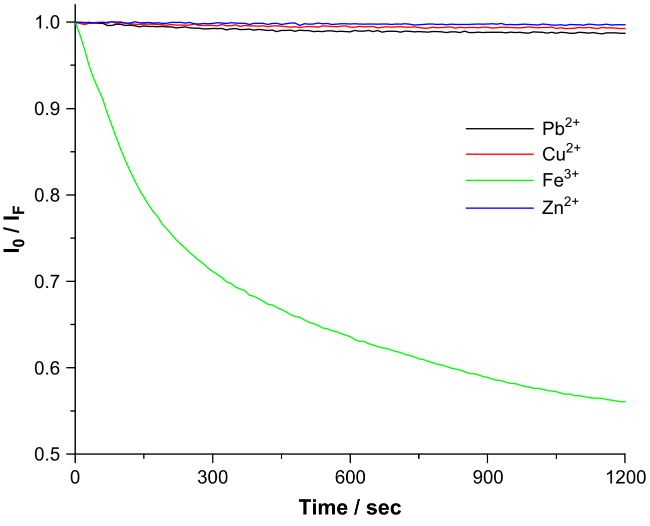


Fig. 4. Changes in the fluorescence emission of poly(St-*co*-MD) film in the presence of different metal cations in buffered, aqueous solution ($CH_3COOH/NaCH_3COO^-$ at pH = 5.0).

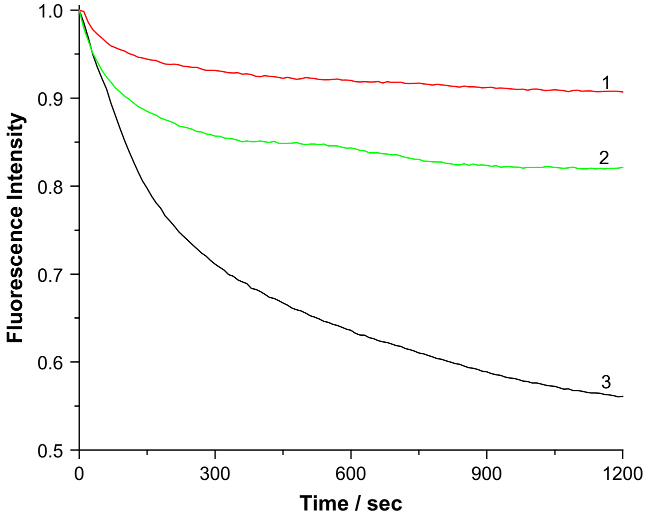


Fig. 5. Changes in the fluorescence emission of poly(St-*co*-MD) at different concentrations of Fe^{3+} cations: 1 (5×10^{-6} mol l^{-1}); 2 (5×10^{-5} mol l^{-1}); 3 (1×10^{-4} mol l^{-1}) in buffered aqueous solution ($CH_3COOH/NaCH_3COO^-$ at pH = 5.0).

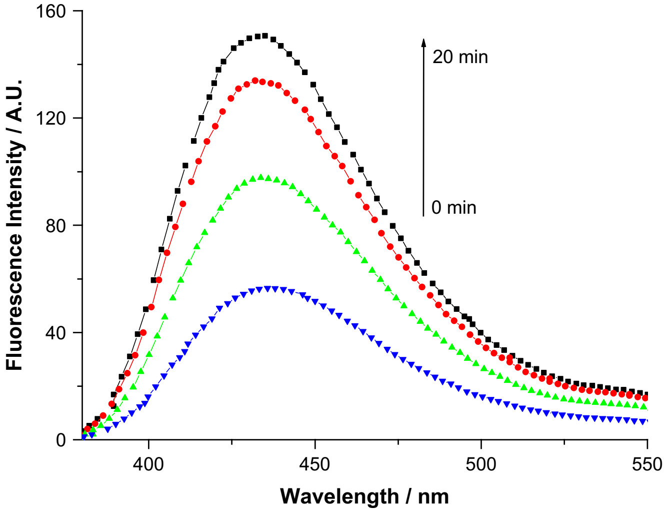


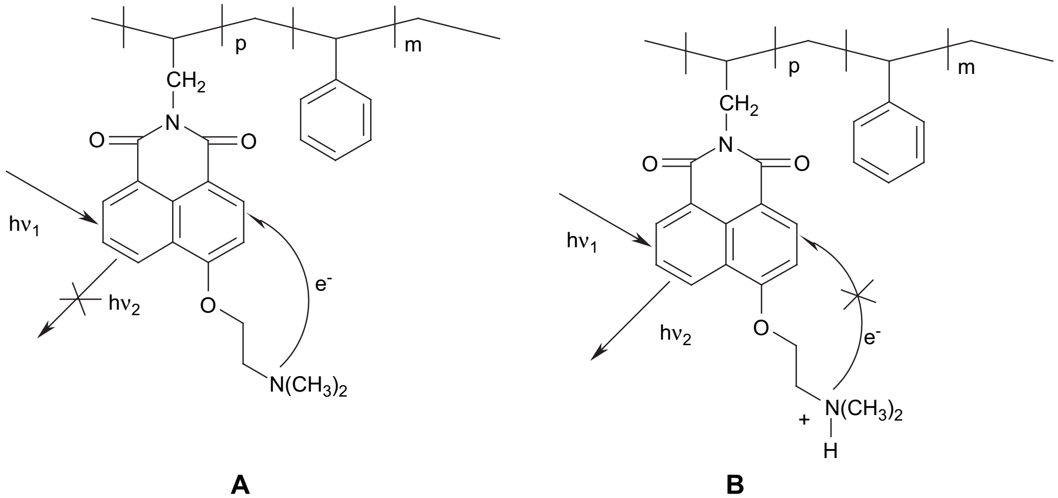
Fig. 6. Fluorescence spectra of poly(St-*co*-MD) at intervals of contact with an aqueous solution at pH 5.0.

two systems as well as the different nature of the solvents used. In the solid state, the rigidity of the 1,8-naphthalimide fluorophore after its bonding to the main polymer chain blocks the formation of a complex between the metal cation and the nitrogen receptor atom in MD. Thus, the Fe^{3+} cations may have reacted with the carbonyl groups or the p-electrons of the aromatic MD rings which lowered fluorescence intensity [6].

Fig. 5 shows the changes in the fluorescence intensity of poly(St-*co*-MD) for three different concentrations of Fe^{3+}; the fluorescence quenching was 10% at 5×10^{-6} mol l^{-1}, 19% at 5×10^{-5} mol l^{-1} and 45% at 1×10^{-4} mol l^{-1}. These findings reveal the potential of poly(St-*co*-MD) as an effective and selective heterogeneous sensor for detecting Fe^{3+} in aqueous solutions.

3.4. Effect of protons on the spectral properties of the polymeric sensors in the solid state

The fluorescence intensity of monomeric 1,8-naphthalimide in aqueous solution was strongly dependent on the pH of the medium. As intensive fluorescence was observed at pH < 6.5 [10], it was considered interesting to follow the behaviour of the solid polymer film in acidic aqueous media (H_2SO_4). The changes with time in the fluorescence spectra of poly(St-*co*-MD) in aqueous acidic solution at pH 5 are presented in Fig. 6. The fluorescence emission increased with increasing time of contact with the aqueous acidic medium. The slight hypsochromic shift (4 nm) of the fluorescence maximum is evidence of the good interaction between the copolymer and the protons from the aqueous medium,



Scheme 3. Proposed mechanism for the fluorescence enhancement of poly(St-*co*-MD) in acidic media.

thus the fact showing the potential of the poly(St-*co*-MD) to serve as a heterogeneous sensor for detecting protons in water sources.

The higher fluorescence intensity is due to quenching of PET by the acidic medium. The PET process in the copolymer system travels from the alkylated nitrogen atom of the substitutent through the ethylene spacer towards the 1,8-naphthalimide. Thus the fluorescence of 4-alkoxy-1,8-naphthalimide fluorophore is quenched (Scheme 3A); protonation of the dimethylamino group stops electron transfer and restores fluorescence of the fluorophore (Scheme 3B).

4. Conclusions

While monomeric 1,8-naphthalimide in acetonitrile responds to the presence of metal cations (Zn^{2+}, Pb^{2+}, Cu^{2+} and Fe^{3+}) via significant enhancement of its fluorescence intensity, in a nonpolar medium (tetrahydrofuran in this case) the response was negligible, regardless of the nature of the cations added. These characteristics enabled its use in the synthesis of high M_r sensors; in this context, the new polymeric sensor based on the above chrompophore displayed blue fluorescence that was very sensitive to metal cations. In the solid state, the chemosensor reacted selectively to the addition of Fe^{3+} cations via PET. Moreover, the fluorescence intensity of this high M_r sensors increased in acidic media due to protonation of the *N*,*N*-dimethylamino receptor groups, suggesting that it may offer potential as a reusable sensor for water pollution by Fe^{3+} cations and protons.

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